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WATER-BASED INK COMPOSITE

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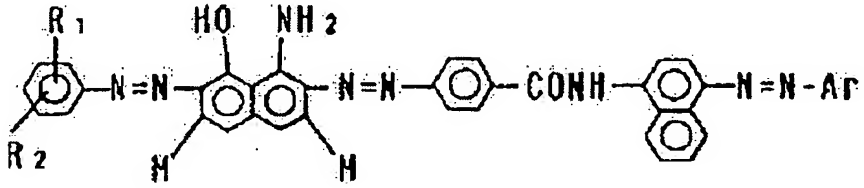
[There are no amendments to this patent.]

Claim

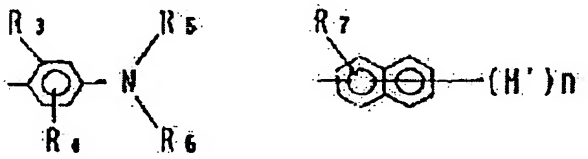
A water-based ink composite characterized by containing at least one water-soluble dye expressed by the general formula below:

Formula



(R_1, R_2: Hydrogen, alkyl group, alkoxy group, hydroxyalkyl group, halogen, carboxyl group or its salt, sulfonic acid group or its salt, cyano group, amino group, carbamoyl group, sulfamoyl group, and nitro group,

M: Sulfonic acid group or its salt,

Ar: 

R_3: Hydrogen, hydroxyl group, alkyl group, and amino group,

R_4: Hydrogen, alkyl group, alkoxy group, halogen, carboxyl group or its salt, sulfonic acid group or its salt,

R_5, R_6: Hydrogen, alkyl group, hydroxyalkyl group, and cyanoalkyl group,

R_7: Hydrogen, hydroxyl group, and amino group,

M^-: Same as the aforementioned M

N = 1 or 2).

Detailed explanation of the invention

Field of the technology

This invention concerns a watercolor ink composite, particularly a watercolor ink composite that is suitable for inkjet recording

Prior art

In inkjet recording, it is necessary for the ink that is used to satisfy the conditions below to maintain satisfactory recording over a long period of time.

1) To have the ink properties of viscosity, surface tension, specific conductivity, and density within the appropriate range in accordance with the droplet generating method and the droplet ejection direction control method.

2) To avoid precipitation through a chemical change, or a change in the ink properties while in storage for a long period of time, in use for a long period of time, or during recording inactivity.

3) To have a sufficiently high contrast and sharpness of picture images that are recorded

4) To have a fast drying of printed picture images.

To satisfy the requirements above, a sufficiently high molecular absorption coefficient of the dye used in the ink and a sufficiently high solubility of the dye in water and the wetting agent are required.

Also:

5) The recorded picture images naturally must be sharp picture images without blurring, and must have high waterfastness, lightfastness, and abrasion resistance.

To satisfy the requirements above, several suggestions have been made so far for inkjet recording inks. However, under present circumstances, one that sufficiently satisfies all of the aforementioned conditions has not been obtained yet.

Among the materials that are prescribed in the ink, the above required characteristics are in particular affected by the dye, and the development of a new dye to satisfy these requirements has been long awaited.

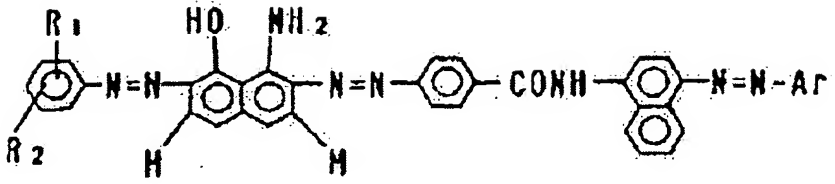
Objective

The objective of this invention is to offer a watercolor ink composite, particularly an inkjet recording watercolor ink composite, in which the conventional problems are solved. In more detail, the objective is to offer a watercolor ink with an excellent ejection characteristic without clogging, and in particular has excellent sharpness, waterfastness, and lightfastness of printed images.

Constitution

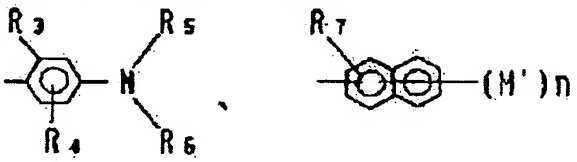
The inventors of this invention have discovered that the use of a specific dye results in a sufficient effect as a measure for solving the aforementioned problems, thus this invention was completed. More precisely, a watercolor ink composite characterized by containing at least one water-soluble dye expressed by the general formula below.

Formula



(R_1, R_2: Hydrogen, alkyl group, alkoxy group, hydroxyalkyl group, halogen, carboxyl group or its salt, sulfonic acid group or its salt, cyano group, amino group, carbamoyl group, sulfamoyl group, and nitro group,

M: Sulfonic acid group or its salt,



Ar:

R_3: Hydrogen, hydroxyl group, alkyl group, and amino group,

R_4: Hydrogen, alkyl group, alkoxy group, halogen, carboxyl group or its salt, sulfonic acid group or its salt,

R_5, R_6: Hydrogen, alkyl group, hydroxyalkyl group, and cyanoalkyl group,

R_7: Hydrogen, hydroxyl group, and amino group,

M': Same as the aforementioned M.

N = 1 or 2).

In the above, desirable cations that form a sulfonic acid salt or a salt of carbonic acid include Li^+, K^+, Na^+, and quaternary ammonium, for example.

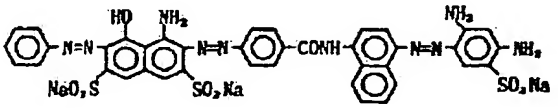
The content of the dye expressed by the aforementioned general formula is 0.5-20.0 parts by weight per 100 parts by weight of the ink, desirably 1.5-6.0 parts by weight. The effect as a dye decreases when it is less than 0.5 wt section, and the density of picture images that are obtained becomes insufficient. Precipitation occurs in the ink when exceeding 20.0 parts by weight and after a long period of time has passed, and a sufficient ink jet recording is not obtained.

To adjust the color tone and obtain a black color, additional blue, red, and yellow dyes can be used in combination with the dye of this invention. Dyes that can be used in combination with blue colors include CI Direct Blue -1, -8, -71, -76, -86, -108, -200, -201, -202, and 236, CI acid blue 1, -7, -9, -15, -175, and 249, for example; with red dyes, CI direct red 1, -9, -15, -17, -28, -37, -62, -75, -81, -83, -89, -99, -220, -225, and 227, CI Acid Red 35, -44, -52, -82, -92, -94, -115, -131, -134, -154, -186, -249, -254, and 289, for example; with yellow dyes, CI Direct Yellow 12, -27, -28, -33, -39, -44, -50, -58, -85, -86, -87, -88, -100, -110, -142, and 144 and CI

Acid Yellow 7, -17, -23, -42, -44, -79, -99, and -142, for example, as well as CI Direct Orange 26, and CI Reactive Blue 2, for example.

The following is a list of detailed examples of dyes that can be used in the watercolor ink composite of this invention.

(1)



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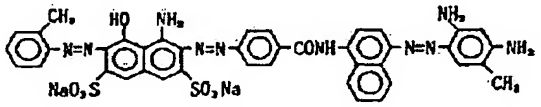

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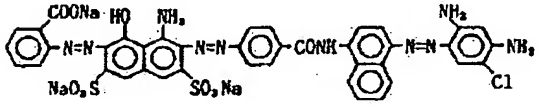

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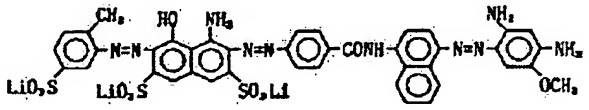

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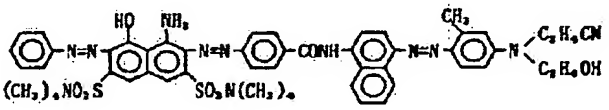

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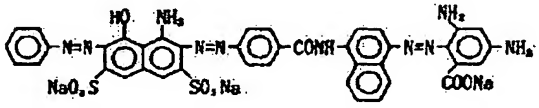
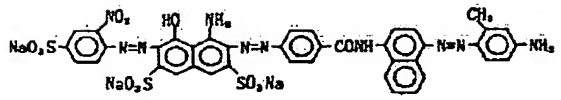
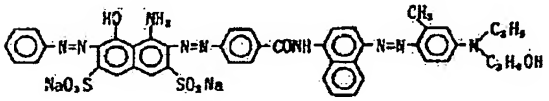
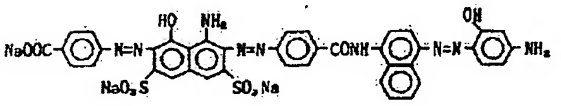
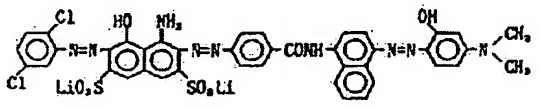
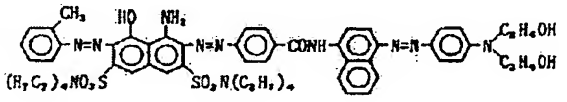


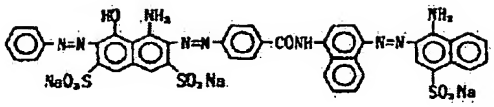
(7) 

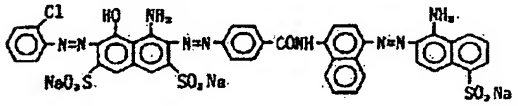
(8) 

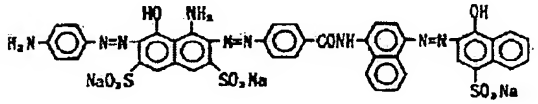
(9) 

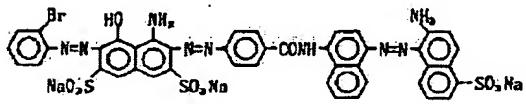
(10) 

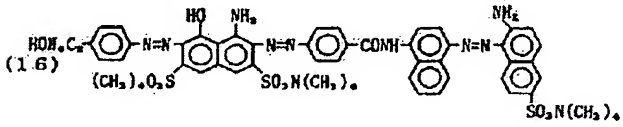
(11) 

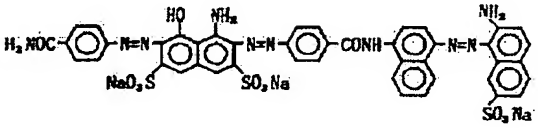
(12) 

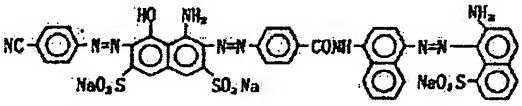
(13) 

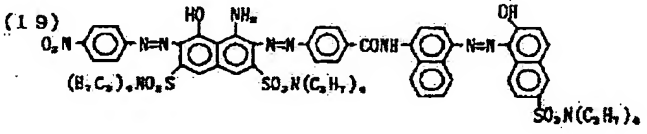
(14) 

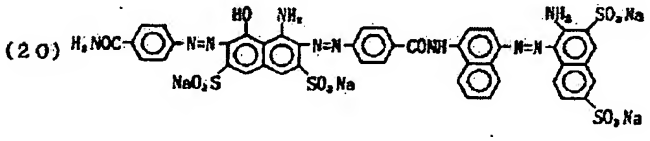
(15) 

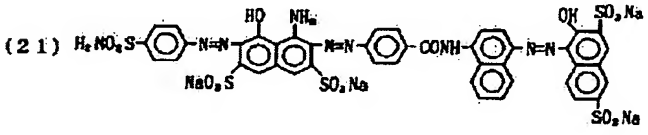
(16) 

(17) 

(18) 

(19) 

(20) 

(21) 

Next, the manufacturing method of these dyes will be explained by the dye in Detailed Example (1).

2.8 g (0.01 mol) of N-(4-aminobenzyl)-1,4-naphthaleneamine are dissolved in 150 mL of water and 7 mL of concentrated hydrochloric acid, 15 mL of a 10% aqueous sodium nitrite solution are added at 10°C or below for diazotization. After stirring for 30 min, a small amount of sulfamic acid is added, and the nitrous acid that remains is removed.

3.8 g of H acid are added to 150 mL of water, 2 g of sodium acetate are added to this and dissolved. This H acid solution is added to the previous diazo-solution all at once, reacted at 10°C for 20 h, and a monoazo dye solution of the color red is obtained.

1.9 g of m-phenylene diamine-4-sulfonic acid are added to this monoazo dye solution, 7 g of sodium acetate are gradually added, and the pH is adjusted to 4-5. Then, a diazo dye solution of the color red is obtained after reaction at 35°C for 10 h. Next, 13 g of sodium carbonate are added to this diazo dye solution to alkalinize it, and it is then cooled 5°C or below. Into this, a solution in which 1 g of aniline is diazotized is slowly added and reacted for 1 h. 80 mL of concentrated hydrochloric acid are added to this reaction solution for strong acidification, and the black-colored dye that has precipitated is collected by filteration. This black-colored dye is washed 3 times with 300 mL of methanol to eliminate the inorganic salt, then dissolved in 150 mL of an aqueous sodium hydroxide solution in equivalent amount, the water is evaporated and it is dried to a solid, and 9.5 g of the dye indicated in Detailed Example (1) as a black powder are obtained.

Water is used as the solvent component in the ink of this invention. However, water can also be mixed with any of the following water-soluble organic solvents for purposes such as adjusting the ink property to a desired value, preventing the ink from drying, and for improving the solubility of the color, for example.

Examples include polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, and glycerin, for example, alkyl ethers of polyhydric alcohols, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether, for example, and additionally, N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethyl imidazolidinone, dimethyl formamide, and triethanol amine, for example.

Among these, diethylene glycol, polyethylene glycol 200-600, triethylene glycol, ethylene glycol, glycerin, and N-methyl-2-pyrrolidone, for example, are particularly desirable. The effect of obtaining a high solubility of the dye and preventing clogging by preventing the evaporation of water content can be obtained by using these.

The aforementioned water-soluble organic solvent in the ink can be used in the content within a range of 5-80% of the total amount of the ink, however, the use in a range of 15-60% is desirable from viewpoints of the viscosity and the drying performance.

Conventionally known additives been can be added to the ink of this invention in addition to the aforementioned dyes and solvent.

For example, as preservatives, sodium dehydroacetate, sodium sorbate, sodium 2-pyridinethiol-1-oxide, sodium benzoate, and sodium pentachlorophenol, for example, can be used in this invention.

As a pH adjustor, optional materials can be used if they can control the pH of the ink within the range of 9.0-11.0 without negatively affecting the ink that is prepared.

Examples include amines, such as diethanolamine and triethanolamine; hydroxides of alkali metal elements, such as lithium hydroxide, sodium hydroxide, and potassium hydroxide; ammonium hydroxide, quaternary ammonium hydroxide; and alkali metal carbonates, such as lithium carbonate, sodium carbonate, and potassium carbonate.

Examples of chelating agents include ethylenediamine tetraacetic acid sodium salt, nitrilotriacetic acid sodium salt, hydroxyethylethylenediaminetriacetic acid sodiumsalt, diethylenetriaminepentaacetic acid sodium salt, and uramildiacetic sodium salt.

Examples of anticorrosion include sodium sulfate, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, and dicyclohexylammonium nitrite.

Additionally, a water-soluble ultraviolet absorber, water-soluble infrared absorber, water-soluble high-molecular compound, dye-solubilizing agent, and surfactants, for example, can be added in accordance with the purpose.

Application examples and comparative examples of this invention will be indicated below. All % is weight %.

Application Example 1

The composites below are heated to about 50°C, stirred and dissolved, then filtered through a Teflon filter with a pore diameter of 0.22 μm, and ink is prepared.

Dye from Detailed Example (1):	3.0%
Diethylene glycol:	15.0%
N-methyl-2-pyrrolidone:	15.0%
Sodium dehydroacetate:	0.2%
Water:	66.8%

Inks in Application Examples 2-5 and Comparative Examples 1-3 are prepared in the same manner as in Application Example 1 except for using the materials of the compositions below.

Application Example 2

Dye from Detailed Example (5):	3.0%
Polyethylene glycol 200:	15.0%
Triethylene glycol monomethyl ether:	5.0%
Sodium dehydroacetate:	0.2%
Water:	76.8%

Application Example 3

Dye from Detailed Example (8):	3.0%
Diethylene glycol:	20.0%
1,3-dimethylimidazolidinone:	5.0%
6-acetoxy-2,4-dimethyl-m-dioxane:	0.3%
Water:	71.7%

Application Example 4

Dye from Detailed Example (12):	3.0%
Diethylene glycol:	20.0%
Glycerin:	20.0%
6-acetoxy-2,4-dimethyl-m-dioxane:	0.3%
Water:	71.7%

Application Example 5

Dye from Detailed Example (15):	3.0%
Polyethylene glycol 200:	15.0%
Triethylene glycol monomethyl ether:	5.0%
Sodium 2-pyridinethiol-1-oxide:	0.3%
Water:	76.7%

Application Example 6

Dye from Detailed Example (16):	3.0%
Diethylene glycol:	15.0%
N-methyl-2-pyrrolidone:	15.0%
Sodium dehydroacetate:	0.2%
Water:	66.8%

Application Example 7

Dye from Detailed Example (18):	3.0%
Diethylene glycol:	20.0%
Glycerin:	5.0%
6-acetoxy-2,4-dimethyl-m-dioxane:	0.3%
Water:	71.7%

Comparative Example 1

Direct Black-32:	3.0%
Diethylene glycol:	15.0%
N-methyl-2-pyrrolidone:	15.0%
Sodium dehydroacetate:	0.2%
Water:	66.8%

Comparative Example 2

Acid Black-2:	3.0%
Polyethylene glycol 200:	15.5%
Triethylene glycol monomethyl ether:	5.0%
Sodium dehydroacetate:	0.2%
Water:	76.8%

Comparative Example 3

Food Black-2:	3.0%
Diethylene glycol:	20.0%
Glycerin:	5.0%
6-acetoxy-2,4-diethyl-m-dioxane:	0.3%
Water:	71.7%

Application Examples 1-7 and Comparative Examples 1-3 are tested for the following, and Table 1 shows the results.

1) Sharpness of picture images

An inkjet printer for a word processor Report 5600J manufactured by Ricoh is loaded with the prepared inks, and printings are obtained.

Inks that give vivid picture images are indicated by O in Table 1.

2) Lightfastness of picture images

Picture image samples obtained in 1) are run through a fade meter (Carbon arch lamp, 63°C) for 3 h; the density of the picture image before and after the irradiation by light is measured by a Macbeth densitometer, and the lightfastness (color fading ratio) is obtained by the equation below.

Fading ratio (%)

= 1-(Density of the picture image after irradiation by light/Density of the picture image before irradiation by light) x 100

3) Waterfastness of picture images

Picture image samples obtained in 1) are soaked in water at 30°C for 1 min, the density of the picture image before and after soaking is measured by a Macbeth densitometer, and the waterfastness (color fading ratio %) is obtained from the same equation as the equation in section 2).

4) Shelf life

Ink is placed in a polyethylene container, stored under the respective conditions of -20°C, 4°C, 20°C, 50°C, and 70°C for 3 months. The change in viscosity, surface tension, and electric conductivity, and the presence of a precipitate before and after storage are checked. Table 1 indicates with O those that have no change in properties and no generation of a precipitate when stored under any conditions.

5) Nozzle clogging test

After printing in 1), it is left standing at 20°C in an environment of 65% RH while printing is inactive for 2 months. Then the ability to print normally after it is left standing is evaluated. Three printers are used and tested for each ink sample.

Table 1 indicates normal printing in all 3 printers as O, normal printing not possible in 1 or 2 out of 3 printers as X, and normal printing not possible in all 3 printers as XX. The 5600 J printer is equipped with a device that automatically detects any significant change in the jet ejection direction compared to before it was left standing, and when the nozzle is clogged and ejection is not possible, and it stops the operation of the printer.

Table 1

		③画像の鮮明性	④耐光性（褪色率%）	⑤耐水性（褪色率%）	⑥保存性	ノズル詰り⑦
①	実施例1	○	5	8	○	○
	〃 2	○	5	7	○	○
	〃 3	○	6	7	○	○
	〃 4	○	5	8	○	○
	〃 5	○	8	8	○	○
	〃 6	○	8	8	○	○
	〃 7	○	5	7	○	○
②	比較例1	○	3	7	低温で沈殿	⑧XX
	〃 2	○	5	35	○	○
	〃 3	○	7	45	○	○

Keys: 1 Application Example ___
2 Comparative Example ___
3 Sharpness of picture images
4 Lightfastness (color fading ratio %)
5 Waterfastness (color fading ratio %)
6 Shelf life
7 Precipitates at low temperature
8 Clogging of the nozzle

Effect

The watercolor ink composite of this invention, as clarified in the explanation above, has significant effects, such as excellent ejection characteristic with no clogging, and excellent sharpness, waterfastness, and lightfastness in the picture images that are obtained using this watercolor ink.